SYNLETT

Spotlight 51

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Cerium(III) Chloride Heptahydrate: $CeCl_3·7H_2O$

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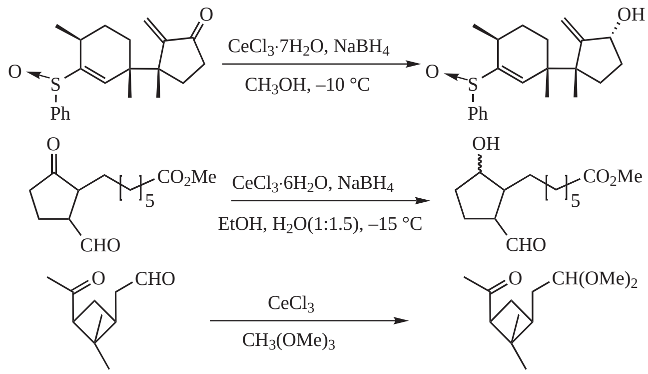
Introduction

Few areas of synthetic chemistry have witnessed a growth as explosive as that brought about by the application of lanthanide reagents to organic synthesis. Cerium(III) chloride heptahydrate[1] is a commercially available lanthanide reagent which is water tolerant, non-toxic, easy to handle, inexpensive and can be used without further purification.

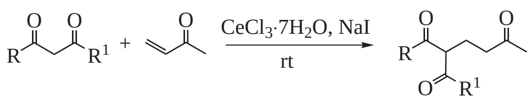
Luche[2] introduced this reagent in 1978 for the selective 1,2 reduction of enones. Since the preparation of organocerium compounds by Imamoto and co-workers[3] in early 1980's these are now widely applied as the reagent of choice to facilitate nucleophilic addition reactions. Recently, Bartoli and co-workers[4] demonstrated the reactivity of $CeCl_3·7H_2O$ in combination with NaI for several organic transformations.

Abstracts

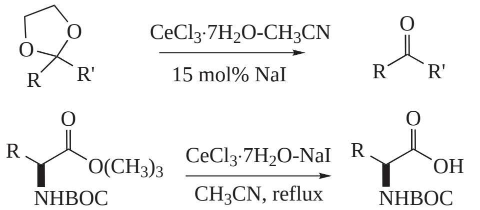
A) Luche[2] used the combination of $CeCl_3$ and $NaBH_4$ for selective reduction of conjugated aldehydes and ketones to allylic alcohols. This procedure has general utility and has been embraced by the synthetic organic chemistry community for 1,2 reduction of enones where other reagents (eg. DIBAL-H, $LiAlH_4$, $Zn(BH_4)_2$ or $NaBH_4$ alone) failed to provide the described products or gave inferior results.
Similarly, selective reduction of ketones in the presence of aldehydes[5] and selective ketalization of aldehydes in the presence of ketones[6] were also very effective using $CeCl_3$. In another report, reduction of conjugated cyclohexenones was achieved using $NaBH_4$–$CeCl_3·7H_2O$ in aliphatic alcohols.[7]



B) Cerium(III) chloride was shown to catalyze the Michael addition[4] of 1,3 dicarbonyl compounds to α,β-unsaturated ketones and α,β-unsaturated aldehydes in the presence of NaI. The catalyst system can be easily separated from the reaction mixture and it can be reused without an appreciable loss of activity. The reactions can also be performed without solvents under microwave irradiation.[8]



C) Cerium(III) chloride is a novel reagent for the nonaqeous selective conversion of dixolane to carbonyl compounds.[9,]
Similarly, $CeCl_3·7H_2O$–NaI in acetonitrile has been recently reported for the selective deprotection of the *tert*-butyl esters in the presence of *N*-Boc protecting group.[10]



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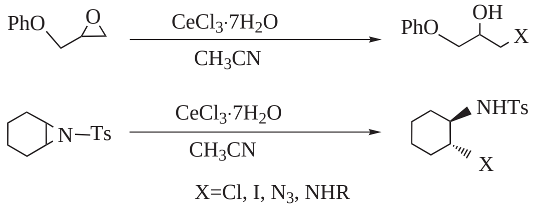
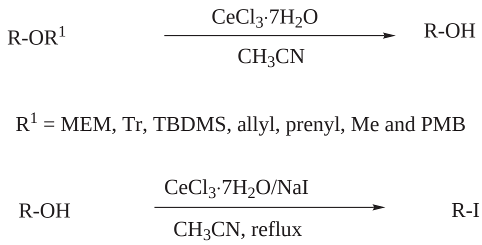
D) Highly regioselective ring opening of epoxides and aziridines has been carried out using cerium(III) chloride to synthesize the corresponding chlorohydrins,[11] iodohydrins,[11] 1,2-azidoalcholols,[12] 1,2-aminoalcohol,[13] chloroamines,[11] iodoamines[11] and 1,2-azidoamines.[12]

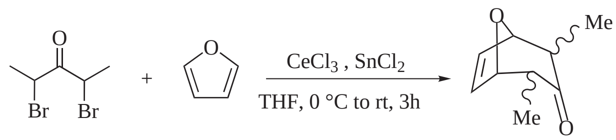


E) Cerium(III) chloride has been used as a mild Lewis acid, and efficient catalyst for the deprotection of alcohol protecting groups such as MEM,[14] Tr,[15] TBDMS,[16] allyl,[17] prenyl,[18] Me[18] and PMB.[19,]

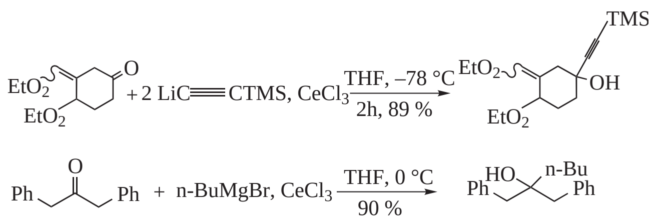
A simple and efficient method for the conversion of alcohols into alkyl iodides[20] using $CeCl_3·7H_2O$–NaI system in acetonitrile has been reported.



F) α,α′-Dibromo ketones react with 1,3-dienes in the presence of $CeCl_3$–$SnCl_2$, providing [3+4] cycloadducts via the oxyallyl cation intermediate.[21]



G) Organocerium reagents[22] are generated in situ by transmetalation reactions from organolithium[23] or organomagnesium reagents.[4] Organocerium reagents are highly oxophilic and significantly less basic than their RLi and RMgBr counterparts.



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